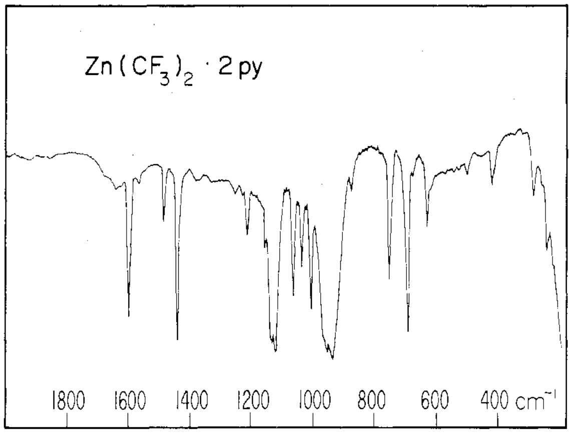

Figure 1. Infrared spectrum of $Zn(CF_3)_2 \cdot 2py$.

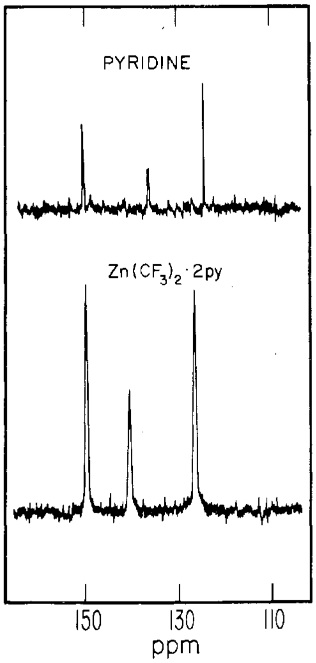

Figure 2. Carbon-13 NMR spectrum of pyridine and $Zn(CF_3)_2 \cdot 2py$ in CD_2Cl_2.

X-ray structural determination have failed.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy. The author would like to thank group CNC-4 of this laboratory for the opportunity to do research as a postdoctoral staff member.

Registry No. $Zn(CF_3)_2 \cdot 2py$, 71672-49-6; $Hg(CF_3)_2$, 371-76-6; $Zn(CH_3)_2$, 544-97-8.

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Crystal and Molecular Structure of $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$, a Neutral, Chelated Four-Coordinate Aluminum Compound, Which Contains Two Types of Al–N Bond

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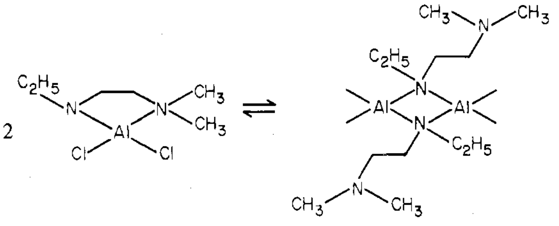
The chemistry of chelated four-coordinate organoaluminum–nitrogen derivatives has been investigated only in recent years,[1,2] and $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ was the first example of this class of compound. In aromatic solvents the compound has been characterized as a monomeric chelate whereas in aliphatic solvents there is an equilibrium between the monomeric chelate and a dimeric species (I). The chemistry of this compound is still not fully understood, especially its behavior as a Lewis base, but the compound is a liquid at room temperature, stunting a structural investigation. To overcome this problem, we obtained the similar substance $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$, and herein we report the results of our structural investigation of this compound.



I

Table I. Crystallographic Details for $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$

mol formula	$Cl_2AlN_2C_6H_{15}$	2θ range	4–50
mol wt	213.1	scan technique	ω-2θ
cryst dimens,	0.40 × 0.50 × 0.60	scan rate, deg min^{-1}	0.3→20.0
cryst system	monoclinic	scan range, deg	0.8 + 0.2 tan θ
space group	$P2_1/c$	scan:bkgd time	2:1
a, Å	7.240 (4)	stds	3 every 50
b, Å	9.667 (5)	no. of data with $F_o^2 > 3\sigma(F_o^2)$	1530
c, Å	16.074 (8)	no. of variables refined	159
β, deg	100.76 (5)	final R	0.031
V, $Å^3$	1105	final R_w	0.032
Z	4	abs coeff, cm^{-1}	6.16
ρ_{calcd}, g cm^{-3}	1.28	std dev of an observn of unit wt	0.652
radiation	Mo Kα (λ = 0.710 69 Å)		

Experimental Section

The title compound, $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$, was kindly supplied by Professor O. T. Beachley, having been prepared by his previously described method.[1] The crystal selected for data collection was sealed in a thin-walled 0.5-mm capillary tube under an inert atmosphere. The final lattice parameters, as determined from a least-squares refinement of the angular settings of 15 reflections accurately centered on an Enraf-Nonius CAD-4 diffractometer, are, along with other relevant crystallographic details, given in Table I. The systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely defined the space group to be $P2_1/c$. Data were collected by the ω–2θ scan technique with graphite-crystal-monochromated molybdenum radiation. One independent quadrant of data was measured to $2\theta = 50°$, leading to 1530 observed $[I > 3\sigma(I)]$ reflections. The structure was solved by application of the direct methods program MULTAN.[3] Refinement of the structure so obtained was carried out by using the Busing and Levy full-matrix least-squares program ORFLS.[4] No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber[5] for Cl, Al,

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(4) Crystallographic programs used on a UNIVAC 1110 include ORFLS (structure factor calculation and least-squares refinement by W. R. Busing, K. O. Martin, and H. A. Levy), ORFFE (distances and angles with esd's by W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), and FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program).

0020-1669/80/1319-0268$01.00/0

Table II. Final Fractional Coordinates and Thermal Parameters[a] for $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0910 (1)	0.1166 (1)	−0.15583 (5)	0.0205 (2)	0.0095 (1)	0.00327 (3)	0.0015 (1)	0.00112 (6)	−0.00022 (5)
Cl(1)	0.1972 (1)	−0.0727 (1)	−0.09899 (5)	0.0359 (2)	0.0125 (1)	0.00437 (3)	0.0066 (1)	0.00094 (7)	0.00092 (5)
Cl(2)	0.2225 (1)	0.1465 (1)	−0.26311 (5)	0.0258 (2)	0.0146 (1)	0.00452 (4)	0.0004 (1)	0.00380 (6)	0.00004 (5)
N(1)	−0.1807 (3)	0.1014 (2)	−0.1978 (1)	0.0220 (5)	0.0106 (3)	0.0040 (1)	0.0005 (3)	0.0015 (2)	0.0000 (1)
N(2)	0.0584 (3)	0.2622 (2)	−0.0934 (1)	0.0245 (6)	0.0117 (3)	0.0041 (1)	0.0008 (4)	0.0011 (2)	−0.0013 (2)
C(1)	0.2422 (6)	0.0557 (4)	−0.2871 (2)	0.0249 (9)	0.0153 (5)	0.0041 (2)	−0.0005 (6)	−0.0003 (3)	−0.0009 (2)
C(2)	−0.2688 (6)	0.0097 (4)	−0.1416 (3)	0.0262 (9)	0.0134 (5)	0.0056 (2)	−0.0013 (5)	0.0037 (3)	0.0005 (2)
C(3)	−0.2382 (5)	0.2491 (3)	−0.1882 (2)	0.0213 (8)	0.0117 (4)	0.0051 (2)	0.0030 (5)	0.0019 (3)	0.0003 (2)
C(4)	−0.1384 (5)	0.3051 (4)	−0.1043 (2)	0.0274 (8)	0.0105 (4)	0.0047 (2)	0.0024 (5)	0.0030 (3)	−0.0005 (2)
C(5)	0.1766 (6)	0.3301 (4)	−0.0220 (2)	0.034 (1)	0.0155 (6)	0.0043 (2)	−0.0003 (6)	0.0010 (3)	−0.0026 (2)
C(6)	0.3771 (7)	0.2913 (6)	−0.0142 (3)	0.031 (1)	0.0028 (7)	0.0072 (3)	−0.0008 (8)	−0.0030 (4)	−0.0038 (4)

atom	x/a	y/b	z/c	B, Å^2	atom	x/a	y/b	z/c	B, Å^2
H(1)[C(1)]	−0.359 (5)	0.056 (3)	−0.302 (2)	5.4 (9)	H(1)[C(4)]	−0.198 (4)	0.271 (3)	−0.058 (2)	3.9 (6)
H(2)[C(1)]	−0.197 (4)	0.115 (3)	−0.324 (2)	5.4 (8)	H(2)[C(4)]	−0.149 (4)	0.406 (3)	−0.109 (2)	4.8 (7)
H(3)[C(1)]	−0.120 (4)	−0.045 (3)	−0.292 (2)	4.5 (6)	H(1)[C(5)]	0.144 (4)	0.311 (3)	0.034 (2)	5.5 (8)
H(1)[C(2)]	−0.228 (4)	0.035 (3)	−0.078 (2)	5.6 (8)	H(2)[C(5)]	0.172 (4)	0.431 (3)	−0.027 (2)	5.8 (8)
H(2)[C(2)]	−0.400 (5)	0.023 (3)	−0.149 (2)	5.8 (8)	H(1)[C(6)]	0.399 (5)	0.194 (4)	−0.005 (2)	6.5
H(3)[C(2)]	−0.227 (4)	−0.089 (4)	−0.152 (2)	6.4 (8)	H(2)[C(6)]	0.453 (5)	0.339 (3)	0.034 (2)	6.5
H(1)[C(3)]	−0.353 (4)	0.252 (3)	−0.189 (2)	4.3 (7)	H(3)[C(6)]	0.435 (5)	0.308 (4)	−0.062 (2)	6.5
H(2)[C(3)]	−0.202 (3)	0.306 (3)	−0.237 (2)	3.9 (6)					

[a] Anisotropic thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

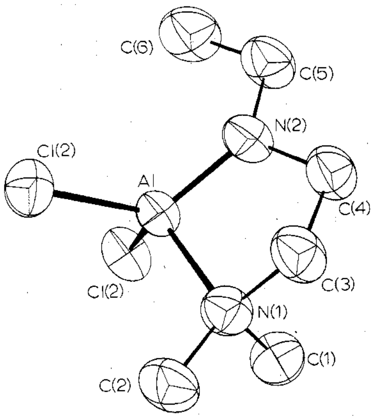

Figure 1. Molecular structure and atom numbering scheme for $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$.

N, and C, whereas for H they were taken from ref 6. Refinement led to the final values of $R = 0.031$ and $R_w = [\sum w(|F_o| - |F_c|)^2/(w|F_o|)^2]^{1/2} = 0.032$.

Results and Discussion

Atomic parameters, distances, and angles are shown in Tables II and III. The most important feature of the structure is the Al–N(2) length, 1.770 (2) Å, which, as can be seen in Table IV, is among the shortest reported aluminum–nitrogen bonds. The inaccuracy of the previously reported structures of compounds containing a short aluminum–nitrogen bond makes the difference between the bond distance observed here and the ones previously reported (0.01–0.02 Å) insignificant. It has previously been suggested that aluminum–nitrogen bonds that fall at about 1.78 Å are in effect double bonds, with dative nitrogen lone pair to aluminum 3d π donation,[1] and, apart from the shortness of the bond, another observation in our structure supports this concept. The virtual planarity[7] of the atoms around N(2) suggests sp^2 hybridization of N(2), with the lone pair being in the remaining 2p orbital, as would be necessary to facilitate the 2p–3d π bond. The delocalization of the N(2) lone pair makes it unlikely that N(2) is a strong base, as had been previously suggested.[2] The other aluminum–nitrogen bond, Al–N(1), at 1.963 (2) Å, falls well within the range commonly observed for aluminum–nitrogen single bonds (1.90–2.02 Å), as shown by Table IV.

Table III. Bond Distances and Bond Angles for $Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$

Distances, Å

Al–N(1)	1.963 (2)	N(1)–C(3)	1.503 (4)
Al–N(2)	1.770 (2)	N(2)–C(4)	1.463 (4)
Al–Cl(1)	2.125 (1)	N(2)–C(5)	1.453 (4)
Al–Cl(2)	2.139 (1)	C(3)–C(4)	1.506 (5)
N(1)–C(1)	1.489 (4)	C(5)–C(6)	1.482 (6)
N(1)–C(2)	1.491 (4)		

Angles, Deg

N(1)–Al–N(2)	91.3 (1)	C(1)–N(1)–C(2)	108.8 (3)
N(1)–Al–Cl(1)	110.0 (1)	C(1)–N(1)–C(3)	110.0 (3)
N(1)–Al–Cl(2)	107.6 (1)	C(2)–N(1)–C(3)	110.2 (3)
N(2)–Al–Cl(1)	121.1 (1)	Al–N(2)–C(4)	112.8 (2)
N(2)–Al–Cl(2)	118.5 (1)	Al–N(2)–C(5)	133.3 (2)
Cl(1)–Al–Cl(2)	106.5 (1)	C(4)–N(2)–C(5)	116.5 (3)
Al–N(1)–C(1)	117.0 (2)	N(1)–C(3)–C(4)	109.7 (3)
Al–N(1)–C(2)	110.6 (2)	N(2)–C(4)–C(3)	107.4 (3)
Al–N(1)–C(3)	99.9 (2)	N(2)–C(5)–C(6)	112.1 (3)

Table IV. Comparison of Al–N Bond Distances

compd	Al–N, Å	ref
$Cl_2AlN(C_2H_5)C_2H_4N(CH_3)_2$	1.770 (2), 1.963 (2)	this study
$LiAl[N{=}C(C_4H_9)_2]_4$	1.78, 1.87	8
$Al[N(SiMe_3)_2]_3$	1.78 (2)	9
$Al_4Cl_4(NMe_2)_4(NMe)_2$	1.79, 1.90, 1.94	10
$[ClAlNC_3H_7]_6$	1.898 (3), 1.914 (3), 1.955 (3)	11
$\{(CH_3)_2Al[N(CH_3){=}C(CH_3)]_2\}_2$	1.923 (1), 1.928 (1)	12
$[(CH_3)_2AlN{=}C(CH_3)_2]_2$	1.925 (2), 1.930 (2)	13
$[(CH_3)_2AlN(CH_3)H]_3$	1.940 (5) av	14
$Cs[Al(CH_3)_3NCS]$	1.944 (10)	15
$K[Al_2(CH_3)_6SCN]$	1.951 (5)	16
$[(CH_3)_2AlN(CH_3)_2]_2$	1.958 (5) av	14
$(CH_3)_5Al_2[N(C_6H_5)_2]$	2.005 (3)	17
$CH_3CNAl(CH_3)_3$	2.02 (1)	18

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The narrow N(1)–Al–N(2) angle, 91.3 (1)°, may have its origin in the 2p–3d π interaction or it may be a consequence of a slight ring strain. However, the latter is not of sufficient magnitude to affect the Al–N bond lengths. All other distances and angles are within expected ranges.

Acknowledgment. We are grateful to Professor O. T. Beachley, Jr., for the sample and the National Science Foundation for support of this research.

Registry No. $Cl_2AlN(C_2H_5)(C_2H_4N(CH_3)_2)_2$, 59738-07-7.

Supplementary Material Available: A listing of structure factor amplitudes and a stereoscopic view of the unit cell packing (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Germanium(II) Dialkoxides

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An understanding of structure and bonding in compounds of the main group elements has evolved with advances in synthetic abilities. For example, exploration of the nonaqueous chemistry of tin(II) compounds in the past few years has been especially fruitful owing to the pioneering efforts and preparative techniques of Morrison and Haendler[1] and others.[2-4] The expansion of germanium(II) chemistry has been noticeably slower. The transient existence of a number of bivalent germanium(II) intermediates has been deduced from sealed tube experiments in which the intermediate is generated and trapped by oxidative addition reactions.[5,6] Relatively few compounds have been fully characterized either because of difficulties in isolating pure substances or because of their thermal, oxidative, or hydrolytic instability. The lag in the development of germanium(II) chemistry is due, in part, to a lack of stable, easily available intermediates and a paucity of information on the physical and spectroscopic properties of these compounds. Thus, the area of bivalent germanium chemistry represents a frontier in the development of an understanding of the behavior of the main group 4 elements. In the present study we wish to report the synthesis and properties of germanium(II) diethoxide which is stable in coordinating solvents. Additionally, we have isolated and characterized a diethanolate complex of germanium(II) diethoxide.

Experimental Section

GeI_2 was synthesized from sublimed GeI_4 by a method described elsewhere.[7] Alcohol was dried over magnesium metal and distilled from magnesium alkoxide under dry nitrogen immediately before use. All other solvents were dried over either sodium metal or phosphorus pentoxide and freshly distilled prior to use. All manipulations were carried out in a glovebag flushed with nitrogen which was predried by passage through several columns of P_2O_5 and deoxygenated through several columns of reduced BTS catalyst (BASF Colors and Chemicals, Inc.).

Table I. Proton NMR Absorptions of Germanium(II) Dialkoxides

	MHz spectrum	temp, °C	δ^a O-CH_2	δ^a -CH_3
$Ge(OEt)_2\cdot xEtOH$ (A)	60^b	30	3.95 q	1.30 t
	60^b	−37	3.95 q	1.15 t
$Ge(OEt)_2{}^d$ (B)	220^c	18	3.95 q, 4.0 br	1.21 t, 1.29 br
		94	4.13 q	1.39 t

[a] Relative to Me_4Si: $J = 7$ Hz for all resolved multiplets; t, triplet; q, quartet; br, broad and unresolved. [b] In C_6H_5Cl. [c] Desolvated under vacuum at ambient temperature for 24 h. [d] In C_6D_6 run with FT mode.

Table II. ^{74}Ge Peaks for the Principal Fragment Ion Clusters of the Mass Spectrum of $Ge(OEt)_2\cdot 2EtOH$ at 80 eV and 90 °C

m/e	%	ion
255	59	$[M - H]^+$
210	6	$[M - EtOH]^{+\cdot}$
209^a	14	$[M - H, EtOH]^+$
165	7	$[M - EtO, EtOH]^+$
164^a	11	$[M - 2EtOH]^{+\cdot}$
149	30	$[M - Me, 2EtOH]^+$
135	15	$[M - Et, 2EtOH]^+$
120	17	$[M - 2EtO, EtOH]^+$
119^a	96	$[M - EtO, 2EtOH]^+$
91	81	$[GeOH]^+$

[a] Corrected for overlapping germanium clusters.

IR spectra were obtained with a Perkin-Elmer 521 double beam spectrophotometer as Nujol and fluorolube mulls between KBr plates. The spectra were calibrated with polystyrene.

Proton NMR spectra were recorded on dilute solutions with a Varian A-60 or HR-220 (FT mode) spectrometer equipped with a variable-temperature probe. All chemical shifts were measured relative to Me_4Si as an internal reference.

Mass spectral fragmentation data were recorded by using a Perkin-Elmer Hitachi RMU-6 mass spectrometer by direct injection of solids into the ionization beam. Thermogravimetric analysis (TGA) was carried out on a DuPont 900 thermal analyzer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Preparation of $Ge(OEt)_2$ Ethanolate Complexes. A 5-g sample of freshly prepared GeI_2 is added to 300 mL of EtOH containing a 3% excess of freshly prepared NaOEt. The yellow diiodide dissolves with loss of color and evolution of heat. The solution is filtered and the solvent is removed under vacuum at 40 °C. The white solid residue is kept under vacuum for 1 h (*extended periods of vacuum storage must be avoided in order to preserve the desired solubility properties*). The product (A) is a free flowing, white powder (2 g) which is soluble in benzene. The byproduct, NaI, is removed by filtration. Table I summarizes the 60-MHz proton NMR spectrum of A at 30 and −37 °C. The absorptions of A move upfield with addition of alcohol. If A is stored under vacuum, it gradually loses solubility in hydrocarbon solvents. The loss of solubility is initially reversible by addition of alcohol but with prolonged vacuum storage the reversibility is lost. The FT 220-MHz spectrum in benzene-d_6 at 18 and 94 °C of this material (B) after vacuum storage for 1 day is reported in Table I. Anal. H/C calcd for $Ge(OEt_2)$, 2.50; found, 2.61.

[†] In partial fulfillment of the requirements for the Ph.D. Degree in Chemistry at the Polytechnic Institute of New York.

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